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Title of Invention: **Deodorant**

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Specifications

1. Title of Invention:

   Deodorant

2. Scope of Patent Claims:

   A deodorant, characterized in that an acidic metal salt is compounded with an organic acid with a high acidity.

3. Detailed Description of the Invention:

Field of Use in Industry

This invention concerns a deodorant; more specifically, it concerns a chemical deodorant for eliminating general odors produced in homes and offices.

Prior Art

In recent years, air conditioning equipment has become common in houses, etc., as they have become more air-tight, and odors produced in homes and offices has become a problem. Various measures have been taken to eliminate these odors.

Masking and physical adsorption have been widely used up to now as methods for eliminating these odors.

The masking method does not actually remove the odor-causing substance, but diminishes the odor or covers it with a stronger odor by the presence of a second substance.

This method is widely use, especially in preventing odors in toilets, but it has the problems that there are great differences among individuals in the odors of the second masking substances that they find desirable and in the persistence of the effectiveness of the method.

Next, the physical adsorption method adsorbs the odorous substance physically by using an adsorbent such as activated carbon, zeolites, etc., and is widely used in refrigerators, automobiles, etc.

This method has the drawbacks that the ability to adsorb ammonia, a common odor-causing ingredient in homes, is low, the adsorptive power is reduced by the absorption of moisture, or the re-release of the adsorbed substances is a concern.

Thus, the deodorizing methods of the prior art have various drawbacks and it is difficult to eliminate odors effectively. Recently, chemical treatment methods, which decompose and remove odors by using chemical reactions, have come into use.

In chemical treatment methods, various chemical substances, such as ferric compounds, potassium permanganate, chlorine compounds, etc., which react chemically with ammonia, amines, hydrogen sulfide, etc., which are common odor-causing ingredients and convert them to odorless substances, have been used.

Problems Which the Invention Seeks to Solve

However, conventional deodorizing methods which use chemical substances have had various drawbacks, in that the reactivities of these substances with the odor-causing substances are low, and sufficient decomposition has not been performed; the reaction rates are slow, and time is required for the decomposition; and their stabilities are poor. Thus, they have not been able to eliminate odors effectively.

This invention was made with this situation in mind, as a result of diligent investigations into the development of stable chemical deodorants which could rapidly and effectively decompose odor-causing substances.

Means for Solving These Problems

That is, this invention is a deodorant which is characterized by the fact that an acidic metal salt is compounded with an organic acid with a high acidity.

Action of the Invention

The deodorant of this invention has the effect of promoting and stabilizing the reactions due to the fact that strong acids produced by the hydrolysis of acidic metal salts and weak bases are co-present with strongly acidic organic acids, the ingredients [of the invention] react with basic or acidic odor-causing ingredients, such as ammonia, amines, hydrogen sulfide, etc., and deodorize them; hydrolysis of the metal salts by the organic acids and formation of complex salts are promoted.

Working Examples

Working Example 1

After 1 liter of an aqueous solution of oxalic acid (30 w/v%) and 1 liter of an aqueous solution of zinc chloride (15 w/v%) were thoroughly stirred and mixed, this mixture was impregnated into granular activated carbon (Nihon Carbon Co., ACG-AM). Next, heating and drying were performed in a vacuum (10 mmHg, 100°C), and a sample in which a deodorant was supported on activated carbon was obtained.

The results of comparing the deodorizing power of this sample with those of activated carbon and zeolite are shown in Table 1.

Table 1

Odor-causing substance / Sample	Ammonia	Hydrogen sulfide	Trimethylamine
Working Example 1	•	O	•
Activated carbon	▪	•	O
Zeolite	O	•	O

• Excellent; O good; • allowable; ▪ not allowable

Working Example 2

After 1 liter of an aqueous solution of oxalic acid (30 w/v%) and 1 liter of an aqueous solution of zinc sulfate (5 w/v%) were thoroughly stirred and mixed,

this solution was absorbed by Japanese paper, after heating and drying were performed in a vacuum in the same manner as in Working Example 1, and a deodorant paper was formed.

The deodorant performance of the deodorant paper formed in this manner was found to be excellent, as in the case of the deodorant supported on activated carbon of Working Example 1.

To explain the make-up of this invention in further detail, deodorizing by means of various kinds of acids was first attempted, since alkaline ingredients such as ammonia and amines are frequently found in common odor-causing substances, but since inorganic acids had various problems, such as the production of stable irritating odors, it was found desirable to use odorless organic acids.

As these organic acids, the deodorizing efficacies of dibasic acids, such as malonic acid, oxalic acid, fumaric acid, succinic acid, and maleic acid, amino acids, such as aspartic acid, glycine, alanine, glutamine, etc., and oxy acids, such as citric acid, gluconic acid, glycolic acid, malic acid, salicylic acid, tartaric acid, etc., were investigated. As a result, it was found that the deodorizing efficacies of the organic acids were related to their acidities, and those of highly acidic ones, such as oxalic acid and maleic acid, were especially good.

However, although the deodorizing efficacies of highly acidic organic acids such as oxalic acid and maleic acid, mentioned above, against alkaline ingredients such as ammonia and amines were excellent, their efficacies against acidic ingredients such as hydrogen sulfide were poor. Therefore, acidic metal salts were next added to the composition, in order to improve the deodorizing efficacy against alkaline ingredients further and to impart a deodorizing efficacy against acidic ingredients.

These acidic metal salts are salts of metals which are bivalent or higher, such as Al, Zn, Mn, Fe, Cu, Ni, Co, Pb, Sn, etc., and strong inorganic acids such as sulfuric acid, nitric acid, hydrochloric acid, etc.

These salts absorb moisture in the air and hydrolyze, producing strong acids such as sulfuric, nitric, or hydrochloric acid and weak bases, which are hydroxides of the bivalent or higher metals mentioned above. The strong acids react with the alkaline ingredients, such as ammonia, amines, etc., in the odor-causing substances and the weak bases react with the acidic ingredients, such as hydrogen sulfide, in these substances, making them odorless.

Although the acidic metal salts all have the effect of eliminating odors, as mentioned above, it is necessary to consider also their chemical stabilities, toxicities, costs, etc. From this point of view, it is desirable to use zinc salts, such as $ZnSO_4$, $Zn(NO_3)_2$, $ZnCl_2$, etc., as the acidic metal salts.

Therefore, as the make-up of this invention, it is most desirable to use oxalic acid or maleic acid as the highly acidic organic acids, and compound sulfuric acid, nitric acid, or hydrochloric acid salts of zinc with them.

Next, Table 2 shows the relationships between the composition ratios of the aforementioned organic acids and zinc salts and the deodorizing efficacy.

Table 2

Deodorant composition ratio		Odor absorption rate (%)	
Oxalic acid	Zinc chloride	NH_3	H_2S
0	1.0	44	40
0.1	0.9	48	40
0.2	0.8	60	40
0.3	0.7	69	46
0.4	0.6	75	50
0.5	0.5	78	55
0.6	0.4	95	9
0.7	0.3	95	92
0.8	0.2	95	92
0.9	0.1	100	94
1.0	0	50	10

As shown in Table 2, although some deodorant efficacy was observed when the oxalic acid or the zinc chloride were used alone, superior efficacies against both the alkaline ammonia and the acidic hydrogen sulfide were shown with the synergistic effect obtained by using both of them together.

As is also clear from this table, especially good deodorizing efficacies are shown with specific composition ratios of the oxalic acid and zinc chloride; therefore, it is desirable for the quantity of zinc chloride in the composition to be in the range of 10–40%.

Finally, there are no particular limits on the forms in which the deodorant is used; one can conceive of aqueous solutions of specific quantities of the organic acid and acidic metal salt, powders obtained by heating and drying these aqueous solutions in a vacuum, adsorbed bodies, obtained by impregnating the aqueous solutions into porous substances such as activated carbon, zeolites, paper, cloth, etc., and then heating and drying them in a vacuum.

Among these forms in which the deodorant can be used, the form in which it is adsorbed on activated carbon, zeolites, etc., is desirable for application in home air conditioners; in this case, the quantity adsorbed is preferably about 10–20 wt% of the activated carbon or zeolites.

This is because a very excellent deodorizing efficacy can be exhibited by also exhibiting the physical adsorption ability of the activated carbon or zeolites which is the support of the deodorant.

Effect of the Invention

The deodorant of this invention has the make-up and action described above; its effect is to effectively deodorize both alkaline ingredients, such as ammonia and amines, and acidic ingredients, such as hydrogen sulfide; it is also chemically stable and exhibits its effect over a long period of time.

Therefore, if the deodorant of this invention is adsorbed on activated carbon or zeolites, it provides a deodorant which has the physical deodorant effectiveness of these substances in addition to the chemical deodorizing effect of the deodorant of this invention, and thus is an excellent deodorant for purifying home air.

Applicant: Janome Sewing Machine Co., Ltd.

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Title of Invention: **Deodorant**

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Specifications

1. Title of Invention:

   Deodorant

2. Scope of Patent Claims:

Claim 1: A deodorant, comprising an aqueous solution of a bivalent iron salt and at least one compound selected from citric acid, malic acid, tartaric acid, maleic acid, fumaric acid, and their salts, dissolved in an aqueous solvent.

3. Detailed Description of the Invention:

This invention concerns a deodorant, the principal ingredient of which is the divalent iron ion.

Deodorants which use the reactivity of the divalent iron ion are already known; for example, deodorants comprising the divalent iron ion and L-ascorbic acid (vitamin C) dissolved in an aqueous solvent are known. However, the L-ascorbic acid used as a stabilizer in this case has the problem that it is expensive.

The inventors performed diligent research to develop an inexpensive stabilizer to replace the L-ascorbic acid used in this case. As a result, they discovered that citric acid, malic acid, tartaric acid, maleic acid, fumaric acid, and their salts are suitable for this purpose, and perfected this invention.

That is, this invention provides a deodorant which comprises an aqueous solution of a bivalent iron salt and at least one compound selected from citric acid, malic acid, tartaric acid, maleic acid, fumaric acid, and their salts, dissolved in an aqueous solvent.

As the bivalent iron salts used in this invention, one can use various ones which are already publicly known; in general, the sulfate, nitrate, or the halides (the chloride, bromide, etc.) are used. On the other hand, as the salts of the aforementioned organic acids which are used in combination with these bivalent iron salts, publicly known ones, e.g., sodium, potassium, or other alkali metal salts are generally used. The proportions in which the aforementioned organic acids or their salts are used are not particularly limited, but at lest 5 parts by weight, preferably 10 or more parts by weight, and especially desirably 200–100 parts by weight are used per 100 parts by weight of the bivalent iron salt. As the aqueous solvent, water is ordinarily used; if desired, suitable quantities of ethanol, propanol, or other water-soluble organic solvents can be added. The concentration of the bivalent iron salt in the aqueous solvent is 0.1 wt% or higher, preferably 1 wt% or higher; its upper limit is the solubility of the bivalent iron salt.

The deodorant of this invention can be used in various pH regions, acidic, neutral, or alkaline, by adding pH regulators (e.g., NaOH, $NaHCO_3$, H_2SO_4, HCl, etc.). In general, deodorants with pH values in the acidic region are used for alkaline odors such as ammonia or amines, and deodorants with pH values in the neutral or alkaline regions are used for hydrogen sulfide or mercaptan odors.

The deodorant of this invention can be used as is, in an aqueous solution, or it can be used as a gel, with a gelling agent added, or it can be impregnated into a

water-absorbent support, e.g., activated carbon, pulp powder, wood powder, sawdust, zeolites, perlite, vermiculite, sepiolite, loess, clay, absorbent cotton, paper, nonwoven fabric, etc.

When the deodorant of this invention comes into contact with odors of ammonia, amines, hydrogen sulfide, mercaptan, etc., under suitable pH conditions, the bivalent iron ion (Fe^{++}) reacts with these odor ingredients and the odors are eliminated.

It is advantageous for the deodorant of this invention to contain a deliquescent substance. In this case, various publicly known deliquescent substances can be used, such as calcium chloride, magnesium chloride, iron chloride, aluminum chloride, potassium hydrogen sulfate, sodium hydrogen sulfate, bittern, raw table salt, etc. The quantity of the deliquescent added is not particularly limited, but in general 0.01–0.5 part by weight, especially 0.05–0.2 part by weight, per 1 part by weight of the bivalent iron salt is used. If the deodorant of this invention is impregnated into a support consisting of a solid substance, this deliquescent can suppress the transpiration of water and prevent the drying of the bivalent iron salt after the water has transpired; it has the effect of giving moisture to the bivalent iron salt and maintaining the reactivity of the bivalent iron salt.

Next, this invention will be explained in further detail by means of working examples.

In order to observed the stabilizing effect of the organic acid or its salt on the bivalent iron ion, 0.5 g of various organic acids or their salts were added to 10 cc of a 10 wt% aqueous solution of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) to make sample aqueous solutions, these solutions were left standing for one month, and the presence or absence of a precipitate was then checked. The results are shown in the following table.

Table 1

Sample No.	Organic acid or its salt	Presence or absence of precipitate
1	3Na citrate $\cdot 2H_2O$	Absent
2	Citric acid	"
3	Sodium malate	"
4	Tartaric acid	"
5	Maleic acid	"
6	Fumaric acid	"
7*	-	Yes

* Comparison example

From the results shown in Table 1 above, it can be seen that the aqueous solutions of this invention are clearly stabilized.

Working Example 2

A solution was made by adding 5 parts by weight 3Na citrate·$2H_2O$, 10 parts by weight ferrous sulfate heptahydrate, and 3 parts by weight crude table salt to 100 parts by weight water and dissolving them homogeneously. Five cubic centimeters of this solution were added to 20 g fine calcined vermiculite powder and mixed thoroughly to impregnate the solution. The result was sealed into an air-permeable bag (8 x 6 cm) to make the product.

Next, one of two products obtained in this way was put into a polyethylene bag with a volume of approximately 1200 cc and a filter paper impregnated with 0.5 cc ammonia was also put into the bag; the bag was then tightly sealed. Moreover, the other product was put into a polyethylene bag with a volume of approximately 1200 cc in the same way and a quantity of hydrogen sulfide gas such that its odor could be perceived was also put into the bag; the bag was then tightly sealed. These bags were left for 18 hours, after which they were opened and the odors in them were investigated. It was found that no odor could be perceived in either bag.